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PREDICTION OF THE ENVIRONMENTAL FATE OF PENTACHLOROPHENOL AS A FUNCTION OF pH USING FUGACITY MODELS

W.P. Mortimer
Engineer
Environmental Science Section
Chemical Research Department

ABSTRACT

The Clean Air Program of the Ontario Ministry of the Environment uses a number of criteria to classify pollutants, and to determine the type of emission controls required for a given source of the pollutant. The pollutant's environmental behaviour, including transport, persistence and bioaccumulation, is considered in the classification. These factors can be determined experimentally via field or laboratory studies, or through the use of the Fugacity Level II model if specific data are lacking. The Fugacity model uses the physical, chemical and biological properties of a chemical to estimate its environmental fate. In this report, Fugacity Levels I and II models are applied to pentachlorophenol, the major wood pole preservative used by Canadian utility companies.

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INTRODUCTION

The environmental fate of a chemical depends on its physical, chemical and biological properties, the way in which it is released to the environment, and the inter-media transport mechanisms that play a role in its distribution through the environment. Until quite recently, pollution problems were seen to be media-specific, that is, affecting only the water, or air, or soil to which the pollutant was discharged. Emissions guidelines frequently are set based on allowable human intake assuming single-pathway exposure, such as daily water consumption rates and so on. For many important pollutants, human exposure occurs through several routes simultaneously, and regulatory standards should take this into account, although this rarely happens (Davies, 1986).

The Clean Air Program being developed by the Ontario Ministry of the Environment does consider environmental behaviour--transport, persistence and bioaccumulation--in the ranking system for pollutants, which will determine the type of control required on a given pollutant source. Each of these factors is ranked by a numerical score. (The details of how the scores are assigned are given in Appendix A of the Clean Air Program Discussion Paper (Regulation 308) Ministry of the Environment, November, 1987). These are added to give a total score for each pollutant, to a maximum of 24. When specific field studies or laboratory microcosm studies are lacking for a particular chemical, Fugacity Level II models are the suggested means of estimating its environmental fate. For example, for environmental transport, a high score (4/4) is obtained if the chemical is associated with fine particles when released to the environment; if the vapour pressure is greater than 1 kPa and the water solubility is greater than 100 g/m^3; or if at least two media other than the receiving medium each contain more than 20% of the chemical released, according to a Fugacity Level II model. The score decreases as the vapour pressure, water solubility and/or the proportion of the released chemical partitioning into other media decreases. A score of 0 is obtained if the vapour pressure is 1 kPa or less and water solubility is less than 100 g/m^3 or if less than 5% of the chemical partitions into media other than the receiving medium.

The Fugacity Level II model also gives an estimate of the chemical's environmental persistence. A score of 10/10 is given if the half-life is greater than 100 days, 7/10 if it is between 50 and 100 days, 4/10 for between 10 and 50 days, and 0 if it is less than 10 days. The last environmental fate parameter, bioaccumulation, can be measured directly, or estimated using a correlation with the logarithm of the octanol-water partition coefficient, K_{ow}, the ratio of the concentration of the chemical in octanol to that in water, at equilibrium. The bioaccumulation parameter has a value of 10/10 if log K_{ow} is greater than 6, is 7/10 for log K_{ow} between 4 and 6, is 4/10 for log K_{ow} between 2 and 4, and is 0 if log K_{ow} is less than or equal to 2.

In this report, the use of Fugacity Level I and Level II models will be demonstrated for pentachlorophenol. Pentachlorophenol (PCP) is the major treatment used by utility companies in Canada for the preservation of wood utility poles. Ontario Hydro has approximately 1.5 million wood poles, most of which have been full-length pressure treated with a 5% oil solution of PCP prior to installation, and about a third of these have had a subsequent remedial ground-line treatment with a 10% PCP grease. The preservative tends to migrate down the poles over time, and out into the surrounding soil, where it kills the organisms that cause decay in the wood.

The environmental compartment to which pentachlorophenol, as used by Ontario Hydro, is released, is predominantly soil. The Ontario Ministry of the Environment's Clean Air Program obviously deals with air pollution, but in its method of ranking chemicals according to their environmental behaviour, it can be applied to chemicals regardless of their mode of release to the environment.

FUGACITY MODELS

In highly dilute systems, fugacity, f, is linearly related to concentration. Fugacity has units of pressure (Pa) and can be viewed as the "escaping tendency" of a chemical. Each environmental compartment (air, water, soil, sediment, biota) has a fugacity capacity, Z_i, such that the concentration of chemical in each compartment, C_i, is the product of the fugacity and the fugacity capacity, ie, $C_i = Z_i f$. Fugacity capacities depend on the chemical's properties of vapour pressure, aqueous solubility and octanol-water partition coefficient. Expressions for calculating the fugacity capacity for each compartment are given in Table 1 and are explained in Mackay and Paterson (1981).

TABLE 1

PROPERTIES OF THE PHASES OF THE "EVALUATIVE ENVIRONMENT" USED IN FUGACITY MODELLING

Medium	Volume (m^3)	Density (kg/m^3)	Organic Fraction	Fugacity Capacity, Z ($mol/m^3.Pa$)
Air	6.0×10^9	1.2	0.00	1/RT
Water	7.0×10^6	1,000	0.00	1/H
Soil	4.5×10^4	2,500	0.02	$\frac{0.4\ f_{oc}\ K_{ow}\ \rho}{H}$
Sediment	2.1×10^4	1,500	0.04	$\frac{0.4\ f_{oc}\ K_{ow}\ \rho}{H}$
Biota	7	1,000	0.05	$\frac{0.05\ K_{ow}}{H}$

where R is the ideal gas constant, T is the absolute temperature, H is the Henry's Law coefficient, f_{oc} is the mass fraction of organic carbon in the environmental phase, K_{ow} is the chemical's octanol-water partition coefficient and ρ is the bulk density of the phase.

Fugacity models are based on the concept that differences in the fugacity of a chemical species between environmental compartments drive the transport of the chemical from compartments of high fugacity to those of low fugacity, until equilibrium is reached, and the fugacities in all compartments are equal. For Level I calculations, the conditions are those

of equilibrium, steady-state, and no flow. For Level II, they are also those of equilibrium and steady-state, but advection, photodegradation and biodegradation within the system are also considered.

These models have been applied to an "evaluative environment" proposed by Baughman and Lassiter (1978). No attempt is made to simulate the real environment, but rather, the goal is to obtain information about the relative distributions of the chemical in the various environmental compartments at equilibrium (Mackay and Paterson, 1981). The evaluative environment used in these fugacity models consists of an area 1000 m by 1000 m, with 30% covered by soil to a depth of 15 cm, and 70% by water, to an average depth of 10 m, with 3 cm of sediment, 5 ppm by volume of suspended solids, and 0.5 ppm of biota. The average density and organic carbon content of each phase are listed in Table 1.

Level III and Level IV models are steady-state, non-equilibrium and non-steady-state, non-equilibrium models respectively. They are beyond the scope of this report but descriptions and example calculations can be found in Mackay and Paterson (1982 and 1986). The application of fugacity model concepts to environments other than the general evaluative model has been considered. Mackay et al (1983) describe the Qualitative Air, Water, Sediment Interaction (QWASI) model which is designed for application to a pond or a river environment.

PROPERTIES OF PENTACHLOROPHENOL

CHEMICAL PROPERTIES

Pentachlorophenol is a weak acid with a pKa value, the negative logarithm of the acid dissociation constant, given by various sources as 4.8 to 5.0. When the pH is equal to the pKa, 50% of the acid is in the dissociated form and 50% exists as the acid form. The fraction of PCP in the dissociated form is calculated as $10^{-pH}/ (10^{-pH} + 10^{-pK_a})$. The apparent octanol-water partition coefficient varies with pH. The data of Kaiser and Valdmanis (1982) were used for the calculations contained in this report. The solid phase solubility is also a function of pH, and the values used in the models have been read from the graph of PCP solubility given in Choi and Aomine (1974). The solid phase vapour pressure of 0.015 Pa was obtained from Verschueren (1983). Only the undissociated PCP has any vapour pressure.

PHOTODEGRADATION

Pentachlorophenol photodegrades readily in aqueous solutions. The rate depends on latitude, time of day, time of year and light intensity, as well as on the pH and turbidity of the water (NRC, 1982). Wong and Crosby (1978) found that the rate of photolysis at pH 3 and pH 7 were 5.2×10^{-7} and 2.7×10^{-5} per second respectively. As noted in the NRC report, this 50-fold increase in rate corresponds to a 50-fold decrease in the concentration of the undissociated pentachlorophenol. Increased acidity prolongs the persistence of PCP. The rate constants for photodegradation at different pH values were estimated using the ratio of undissociated fractions of PCP at those pH values. Photolysis is highly depth-dependent, with values of rate constants reported on a cm/day basis. Values of the rate constant are given

(NRC, 1982) for both June and December (17.18 cm/day and 3.25 cm/day) so an average value of 10.2 cm/day was used as an annual rate. The unit world of the fugacity model contains a water portion 700 m long x 10 m deep x 1000 m wide. It is necessary to choose a representative value for the photolysis rate constant that will give an average rate for the entire 10 m depth of the water column. This was achieved by integrating the expression for rate as a function of depth and determining the average photodegradation rate for the water column. The value thus obtained is 0.0703 per day, or 0.00294 per hour, for pH 7.0. Adjusting this value for pH using the ratio of the undissociated PCP fractions at other pH values gives rate constants of 0.00294 x 0.76/0.99 = 0.00226 per hour at pH 5.5, and 0.00294 x 0.9997/0.99 = 0.00297 for pH 8.5. Hwang et al (1987) determined photolysis rates in estuarine and distilled waters for various phenols, under conditions of high irradiance (midday, 30 degrees latitude) at a depth of 3 cm. The degradation constants were much higher than those used here, namely 0.4 per hour at pH 5.5 and 0.7 per hour at pH 10 for PCP in distilled water, but the trend of increasing photolysis with pH is consistent. The photodegradation rate in air is assumed to be zero.

BIODEGRADATION

Biodegradation rates for soil and sediment are very difficult to establish from the literature, for Canadian climatic conditions. In general, the rate of degradation

1. increases with temperature, with an optimum between 24 and 35°C, and is virtually non-existent at either 12°C or 40°C (Martinson et al, 1986);

2. is faster under aerobic than anaerobic conditions (Pignatello et al, 1986);

3. is very dependent on the number of locally adapted microbes (a significant lag time exists before degradation of new sources begins (Pignatello et al, 1986));

4. is strongly influenced by pH (degradation is faster at higher pH conditions (DeLaune et al, 1983));

5. depends on the purity of the pentachlorophenol formulation, soil type, organic and moisture contents (Kaufman, 1978);

6. depends on sediment redox potential (DeLaune et al, 1983); and

7. depends on the concentration, with less than 100 ppm being quickly degraded while greater than 500 ppm, being toxic, shows no degradation (Martinson et al, 1986).

Part of the difficulty in establishing the natural degradation rates stems from the problems encountered in extrapolating laboratory results to field situations. Kirsch and Etzel (1973) stated "...pentachlorophenol...is amenable to biological decomposition under specific idealized laboratory conditions." With all these caveats and conditions in mind, the rate constants for biodegradation in soil and sediments were selected as follows.

Baker et al (1980) found that PCP in soils was slow to degrade, requiring 80-160 days for a 70% decrease in soil concentration for an aerobic soil at pH 7.1. Using an average value of 120 days gives a degradation rate constant of 4.18×10^{-4} per hour. For lack of data, the rate constants for pH 5.5 and 8.5 were estimated to be 4.18×10^{-5} per hour and 4.18×10^{-4} per hour respectively. As the percent dissociated PCP at pH 7.0 and 8.5 are about 99 and 99.97, degradation rates will likely not vary much in this range. At pH 5.5, however, the amount dissociated is 76%, so the difference in pH will likely result in a significant decrease in biodegradation rates.

For sediments, DeLaune et al (1983) found the half-life of PCP to be 19 days at pH 8.5 in a northern U.S. setting. Jones (1984) reported a value of 80 days for pH 3.5-5.5. The half-life at pH 7.0 was estimated to be some intermediate value; 45 days was chosen. Therefore, the selected degradation rate constants in sediments were 1.5×10^{-3} per hour, 6.4×10^{-4} per hour and 3.6×10^{-4} per hour for pH 8.5, 7.0 and 5.5, respectively. Microbial degradation in the water column has not been reported and is assumed to be zero.

The physical, chemical and biological properties of pentachlorophenol used in the fugacity models are summarized in Table 2 for three pH levels of interest, namely 5.5, 7.0 and 8.5.

For the Fugacity Level II model, advective terms for both air and water are required. The values used here were suggested by Dr. D. Mackay (1988, pers. comm.). An input of 100 mol/h was assumed, with an air residence time of 20 days and a water residence time of 100 days (giving a volumetric flow rate for air, G_a, of 1.25×10^{7} m^3/h, and for water, G_w, of 2.92×10^{3} m^3/h). The background air concentration selected for all three cases was one-quarter of the prevailing concentrations determined in the corresponding Level I case. Thus, for pH 5.5, the background concentration in air was chosen to be 4.5×10^{-11} mol/m^3; for pH 7.0, 1.2×10^{-12} mol/m^3; and for pH 8.5, 1.8×10^{-14} mol/m^3.

The background water concentrations were chosen similarly, ie, to be one-quarter of the prevailing water concentrations determined for the Level I case. The values used were, for pH 5.5, 1.1×10^{-6} mol/m^3; for pH 7.0, 2.4×10^{-6} mol/m^3; and for pH 8.5, 2.8×10^{-6} mol/m^3.

The Fugacity Levels I and II models have been formulated as a spreadsheet program. Anyone wishing copies should contact the author.

TABLE 2

PROPERTIES OF PENTACHLOROPHENOL USED IN FUGACITY MODELS

Property	pH 5.5	pH 7.0	pH 8.5
Solid Phase Vapour Pressure (Pa) (Verschueren, 1983)	1.5×10^{-2}	1.5×10^{-2}	1.5×10^{-2}
Total Solid Phase Solubility (g/m^3) (Choi and Aomine, 1974)	3.98×10^{1}	3.16×10^{3}	2.51×10^{5}
Apparent Octanol-Water Partition Coefficient (Kaiser and Valdmanis, 1982)	1.10×10^{4}	2.45×10^{3}	1.23×10^{3}
Photodegradation Rate Constant (h^{-1}) (Wong and Crosby, 1978)	2.25×10^{-3}	2.94×10^{-3}	2.97×10^{-3}
Soil Biodegradation Rate Constant (h^{-1}) (Baker et al, 1980)	4.18×10^{-5}	4.18×10^{-4}	4.18×10^{-4}
Sediment Biodegradation Rate Constant (h^{-1}) (DeLaune et al, 1983; Jones, 1984)	3.6×10^{-4}	6.4×10^{-4}	1.5×10^{-3}

ENVIRONMENTAL FATE OF PENTACHLOROPHENOL

LEVEL I CALCULATION

Partitioning between media changes with pH as shown in Figure 1. At a "system pH" of 5.5, the percent mass in the three top compartments are 31, 44 and 24 for water, soil and sediment, respectively. At a pH of 7.0 (at which 99% of the PCP is dissociated), the mass percents in these compartments are 67, 21 and 12. At a pH of 8.5 these become 80, 13 and 7. As the pH increased from 5.5 to 7.0 to 8.5, the Henry's Law coefficient also decreased, from 0.10 to 0.0013 to 0.000016 $Pa.m^3/mole$. The log K_{ow} value dropped from 4.04 to 3.39 to 3.09, and pentachlorophenol became increasingly a water pollution problem, as less material was sorbed on to soil and sediments.

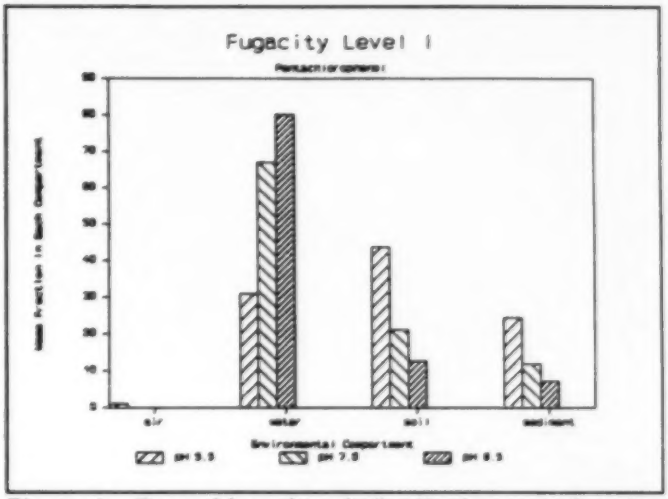

Figure 1. Pentachlorophenol distribution as a function of pH.

LEVEL II CALCULATION

The mass fraction of pentachlorophenol in each of the environmental compartments does not change from the Level I to the Level II calculation. The Level II model does incorporate the mechanisms by which pentachlorophenol is lost from the system, and these change with pH as shown in Figure 2. Advection losses are calculated as the product of the air and water advection rates (from the residence times given on page 6) and the prevailing concentrations in the air and water compartments, respectively.

As the pH increases, the PCP increasingly is found in the water phase, but due to the increasing photodegradation with pH, the loss attributable to advection in the water phase remains about 13.5% for pH 5.5 and 11.6% for the higher pH levels. Advection in the air phase decreases, from 2.3% at pH 5.5 to less than 0.01% at pH 7.0 and 8.5.

At pH 5.5, the most significant reaction (ie degradation, not including advection) occurs in the water, with most (73%) of the total lost via photodegradation. Biodegradation in sediments accounts for 9.4%, and in soil for 2.0%, of the pentachlorophenol lost by the system.

At pH 7.0, the most significant reaction is again photodegradation in water (82%), followed by biodegradation in soil (3.7%) and sediment (3.2%). The situation is similar at pH 8.5, with photodegradation in water accounting for 82.7% of the reaction loss and biodegradation in sediment and soil at 3.8% and 1.9%, respectively.

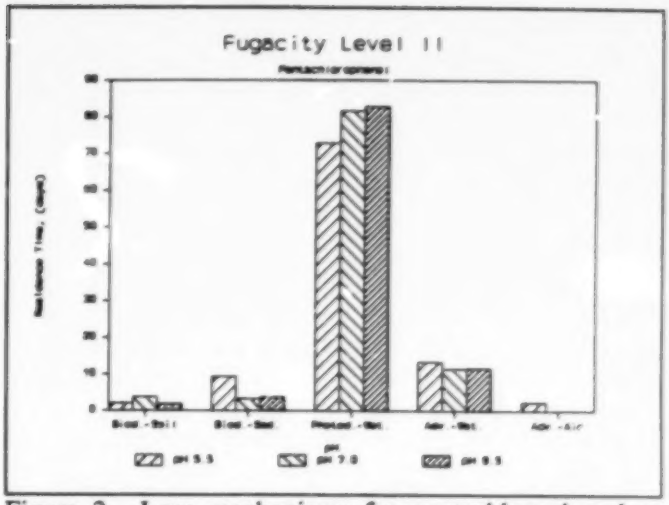

Figure 2. Loss mechanisms for pentachlorophenol as a function of pH.

Overall, the figure shows the major significance of photodegradation losses in the water phase (more than 73% of the total lost is through this route). The next most important loss mechanism is advection in the water phase. Biodegradation in soil and sediment are of minor significance.

The change in residence time with pH is shown in Figure 3. The residence times computed considering advection only (top curve) and reaction only (middle curve) both decrease significantly between pH 5.5 and 7.0 and decrease much less between 7.0 and 8.5. This is due to the fact that the pentachlorophenol is 99% and 99.97% ionized at pH 7.0 and 8.5, respectively so that very little difference is expected in the environmental behaviour between these two pH levels. The overall residence time, considering both advective and reactive losses, decreases from 44.3 days to 17.4 days to 14.6 days as the pH increases from 5.5 to 7.0 to 8.5. (The "persistence" referred to in the Ministry of the Environment's proposed Clean Air Program is that due to reaction only, middle curve). Jury et al (1983) give a soil biochemical half-life of 48 days.

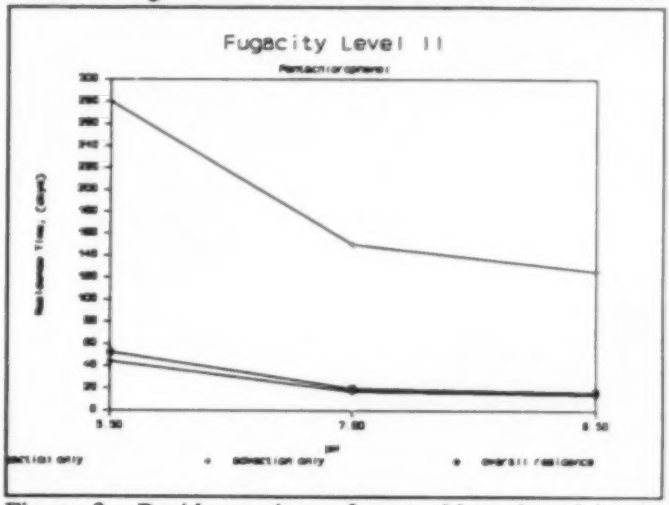

Figure 3. Residence time of pentachlorophenol in the environment, as a function of pH.

DISCUSSION

The ultimate environmental fate of pentachlorophenol is pH dependent, as demonstrated in the previous calculations for the Fugacity Levels I and II models.

The Level II model results can be related to the Environmental Behaviour parameters, described at the beginning of this report. Pentachlorophenol scores 4/4 at pH 5.5, and 3/4 at pH 7.0 and 8.5 in the Environmental Transport category, due to, in the first case, having two compartments (ie, water and sediment) other than the one to which it is released (soil) each having more than 20% of the chemical at equilibrium. At pH 7.0 and 8.5, the solubility of the chemical results in the high transport scores.

The Environmental Persistence parameter has a value of 7/10 for pH 5.5, having a persistence of 55.6 days (at 100 days this parameter increases to 10/10). At the other pH levels, pentachlorophenol scores 4/10 for persistence, being between 10 and 50 days (20 and 16 days for pH 7.0 and 8.5, respectively). Pentachlorophenol is given in the Appendix A of the Green Paper on Regulation 308 as an example of a chemical with a high persistence score (7 to 10).

At pH 5.5, the value of the octanol-water partition coefficient, log K_{ow}, is between 4.0 and 6.0, giving a Bioaccumulation parameter score of 7/10. The K_{ow} value is between 2.0 and 4.0 for the other pH levels, giving a score of 4/10 for them. (The Regulation 308 example gives a Bioaccumulation score of 7 or 10). The total scores for the Environmental Behaviour parameters (out of a possible 24) are 18, 11 and 11 for pH 5.5, 7.0 and 8.5, respectively. This indicates that pentachlorophenol would be considered to have worse environmental transport characteristics, and is more of an environmental hazard under conditions of low pH than under neutral to high pH conditions. In terms of the regulatory system under consideration, the "worst case" of alternative calculations should be chosen, particularly when the variation is due to something as environmentally unpredictable as pH.

CONCLUDING REMARKS

Fugacity models are simple to apply, provided that the physical chemical properties of the chemical in question are available. Much information can be organized through the use of fugacity models, allowing a wide variety of chemicals to be ranked in terms of their predicted environmental behaviour. Other characteristics such as toxicity, route and duration of exposure

must be considered as well when ranking a chemical for pollution control purposes. Regulatory bodies are beginning to recognize the value of a multi-media approach and it is anticipated that the use of fugacity modelling for predicting environmental fate will be more widely adopted in the future.

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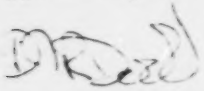
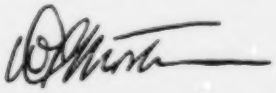


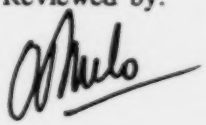
D.J.R. Dodd
Manager
Chemical Research Department

Prepared by:



W.P. Mortimer
Engineer
Environmental Science Section

Reviewed by:



O.T. Melo
Supervising Engineer
Environmental Science Section

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